

Enhanced efficient and sensitive SERS sensing via controlled Ag-nanoparticle-decorated 3D flower-like ZnO hierarchical microstructure

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Various sizes and morphologies of noble metal/zinc oxide hybrid materials have promising applications in surface-enhanced Raman scattering (SERS). Generally, organic agents used during the synthesis of metal nanoparticles will inexorably induce organic pollution on the surface of SERS substrate, resulting in a negative effect on detection sensitivity. Herein, a stable and clean 3D flower-like ZnO/Ag hierarchical microstructure SERS substrate was designed and fabricated via a simple photocatalytic method. This synthetic strategy does not involve usage of any organic agents, which ensures the cleanness and free of impurities interferences. As anticipated, the as-fabricated 3D flower-like ZnO/Ag SERS substrates with high surface-to-volume ratio increased numerous hot spots, and exhibited excellent detection sensitivity to Rhodamine 6G. A linear relationship between the Raman intensity and the concentration of Rhodamine 6G ranging from 10^{-11} to 10^{-4} M was realised. This work demonstrated a performance-enhanced SERS sensor based on microflower-like ZnO@Ag hybrids, which provides a potential method to develop highly sensitive and stable SERS sensor for organic molecules detection.

1. Introduction: Surface enhanced Raman spectroscopy (SERS), by virtue of many advantages such as non-destruction to sample and low sample requirements, presents potential applications in chemical and biomolecular sensing [1–5]. For realising strong and stable signal output, it is crucial to develop SERS-active substrate with high sensitivity. Therefore, various SERS-active substrates have been synthesised by different methods, in general, physical synthesis and chemical synthesis.

Noble metals (e.g. Au, Ag) are widely investigated for their strong electromagnetic enhancement effect, in favour of SERS [6–8]. Unfortunately, the properties of noble metals, such as poor biocompatibility, easy aggregation and oxidation, greatly impeded their practical applications. In order to solve these problems, noble metal/semiconductor hybrid materials show stronger SERS signal benefiting from higher aspect ratio and surface area [9, 10]. Up to now, ZnO with different nano-morphologies has been widely studied [11–15], such as nanorods, nanosheets, nanowires, nanospheres, nanotubes and nanoflowers [16–19]. Especially, Ag nanoparticles supported on ZnO carrier are attractive. Shan *et al.* fabricated the wheatear-like ZnO/Ag composite substrates, which exhibited sensitive SERS activity in detecting Rh6G molecules with the detection limit of 10^{-6} M [20]. Krishna *et al.* reported the ZnO/Ag bilayers and ZnO/Ag/ZnO multilayers, which showed great enhancement of SERS signal with the highest enhancement factor of 7.4×10^6 [21]. However, most of the reported SERS-active substrates are too technologically complex and expensive to realise cost-effective and large-scale production for practical applications. Therefore, there is still a challenge to develop stable, reproducible and sensitive SERS substrate of low cost and convenience for large-scale production.

In this study, a simple and economical approach for fabricating the 3D flower-like ZnO hierarchical microstructure was developed by direct chemical reaction. Using them as an upholder, ZnO/Ag microflowers were synthesised via photocatalytic. The ZnO/Ag microflower hybrids exhibited superior SERS performance benefiting from the cleanness of the substrate surfaces, and the high surface-to-volume ratio with increased number of hot spots. The further electromagnetic field distribution simulation illuminated the excellent SERS activity originated from the nanotips on the ZnO/Ag microflowers and nanogaps among the ZnO petals. This work provides a new approach towards Ag-nanoparticle-decorated

3D flower-like ZnO hierarchical microstructure serving as highly active and stable SERS sensor for organic molecules detection.

2. Experimental

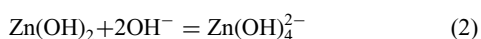
2.1. Chemicals and materials: AgNO₃, KOH, acetone, ethanol, isopropanol and Rhodamine 6G were obtained from Sinopharm Chemical Reagent Co., Ltd. Zn(NO₃)₂•6H₂O was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All solutions were prepared by using Milli-Q water. All chemicals used in the experiments were of analytical grade and used without further purifications.

2.2. Synthesis of 3D flower-like ZnO hierarchical microstructure: Briefly, 2.2 g of KOH was added into 15 ml of 0.32 M Zn(NO₃)₂•6H₂O solution. The mixture was stirred until dissolved. Then, a silicon foil (2 cm × 2 cm) was immersed in the solution. After keeping at 22°C for overnight, the silicon foil was washed with deionised water and dried at 60°C.

2.3. Growth of silver NPs on ZnO carrier with 3D flower-like hierarchical microstructure: The prepared substrates were immersed in 20 ml AgNO₃ aqueous solution with different concentrations (0, 10, 25 and 35 mM) for 0.5 h under sunshine. After that, the samples were washed with de-ionised water and dried at 50°C. The samples were processed in a high vacuum chamber with a base pressure of 5.5 Pa, and the plasma current of 4 mA. The irradiation time was varied between 10 and 50 s.

2.4. Characterisation: The ZnO/Ag microflowers were immersed in Rh6G solutions with different concentrations (from 10^{-4} to 10^{-11} M) and dried before SERS measurement. The Raman spectra was recorded using a confocal microprobe Raman spectrometer (HORIBA, HR Evolution) with a 532 nm laser, with the power of 0.03 mW and the diameter laser spot about 4 μm. The integration duration was maintained for 2 s. ZnO@Ag microflowers were synthesised by ion sputtering apparatus (SBE-12, KYKY). The size and morphology of ZnO/Ag microflowers and ZnO@Ag microflowers were characterised by transmission electron microscope (TEM, HT7700, Hitachi) and scanning electron microscopy (SEM, SU8000). The element analysis was conducted by X-rays of selected areas (EDXA, SU8000).

3. Results and discussion: Fig. 1 presented the schematic design and fabrication diagram for the ZnO carrier with 3D flower-like hierarchical microstructure and ZnO/Ag microflower-like hybrids. The detailed synthesis procedures can be found in the experimental section. In brief, the 3D flower-like ZnO hierarchical microstructure firstly grew on the Si substrate through a modified method. As described in the following reaction:



Next, through the illumination of visible light, Ag nanoparticles were decorated on the surface of ZnO carrier with 3D flower-like hierarchical microstructure.

The SEM images of the synthesised ZnO carrier with 3D flower-like hierarchical microstructure before and after the growth of silver NPs were shown in Figs. 2a and c, respectively. From the images, we can find the ZnO microflowers with a diameter of 2–3 μm . Simultaneously, the morphology of the ZnO microflowers was further characterised by TEM. Fig. 2c showed that the formed ZnO/Ag microflowers possessed high mass production. Fig. 2d further revealed the elemental composition. Zn, Ag and O can be easily found in the EDXA graph. The result suggested that 3D flower-like ZnO/Ag SERS substrates were synthesised by means of in-situ photocatalytic successfully.

The SEM images in Fig. 3 showed the spatial arrangement of Ag NPs on the ZnO microflowers. Ag NPs were attached on the surfaces of the ZnO microflowers randomly. With the concentrations of AgNO_3 aqueous solution increasing, the density of Ag nanoparticles increased, while the size of Ag NPs distributes from 20 to 50 nm randomly. The SERS hot spots are mainly depended on the density of Ag nanoparticles, because the coupling interaction between closely spaced Ag NPs would induce large electromagnetic field.

As described above, ZnO/Ag microflowers can serve as a SERS substrate. In order to check the SERS activity of the ZnO/Ag microflowers, Rh6G dye as the Raman reporter was chosen in this study. In the measurement of SERS spectra, five different areas of ZnO/Ag microflowers were measured per each trial. Fig. 4a shows the SERS spectra with different concentrations of Rh6G ranging from 1×10^{-11} to 1×10^{-4} M. The characteristic Raman spectra of Rh6G are clearly identified even in the Rh6G concentration as low as 10^{-11} M, indicating excellent Raman sensitivity of the ZnO/Ag microflowers. The peaks at 611 and 771 cm^{-1} were

attributed to the C–C–C ring in plane, out-of-plane and C–H in-plane bending vibrations, while the peaks at 1186, 1360, 1508 and 1646 cm^{-1} were originated from symmetric modes of in-plane C–C stretching vibrations [22]. All of Raman spectra were collected over three different spots on the sample and its average was considered for the present study.

Fig. 4b showed the calibration curve between the Rh6G concentration and the Raman intensity of the peak at 1646 cm^{-1} . The logarithmic curve showed an excellent linear relation when the Rh6G concentrations is from 1×10^{-11} to 1×10^{-4} M. The squared correlation coefficient (R^2) was 0.986. The excellent SERS enhancement could be attributed to high aspect

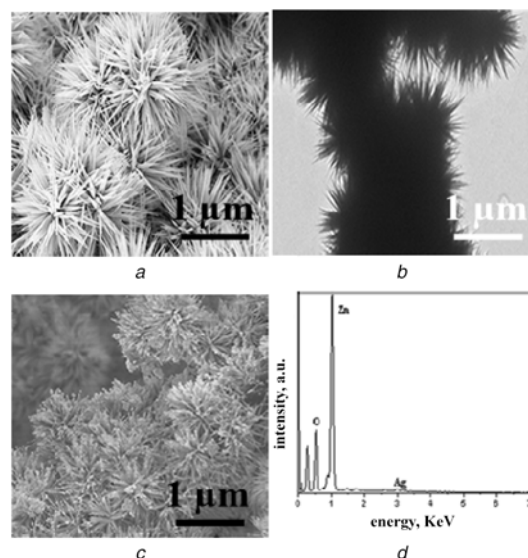


Fig. 2 The SEM and TEM images of samples
a SEM images of ZnO microflowers
b TEM images of ZnO microflowers
c SEM images of ZnO/Ag microflowers
d EDXA spectrum of the ZnO/Ag microflowers

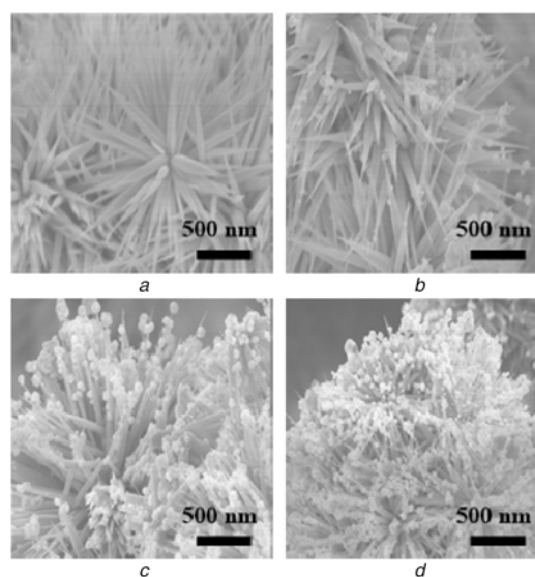


Fig. 3 SEM images of ZnO/Ag microflowers after adding different AgNO_3 concentrations
a 0 mM
b 10 mM
c 25 mM
d 35 mM

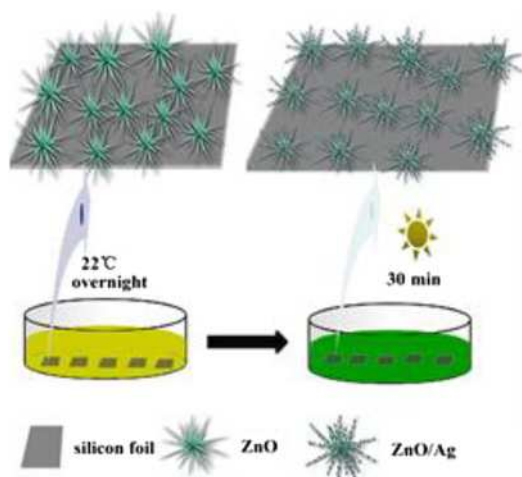


Fig. 1 Synthesis route of ZnO/Ag microflowers

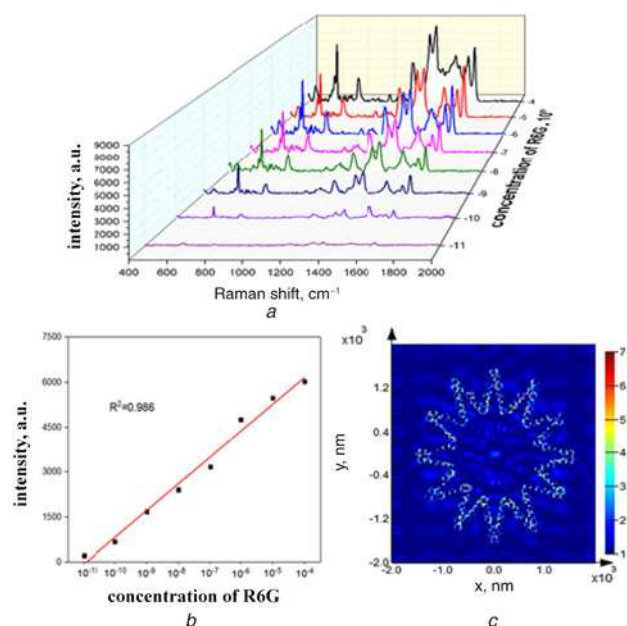


Fig. 4 The SERS spectra and FDTD simulations of samples
 a SERS spectra of Rh6G collected on as-prepared ZnO/Ag microflowers for different concentrations (10^{-4} – 10^{-11} M)
 b Linear relationships between the SERS intensity and the Rh6G concentrations at 1646 cm^{-1}
 c FDTD simulations for ZnO/Ag microflowers

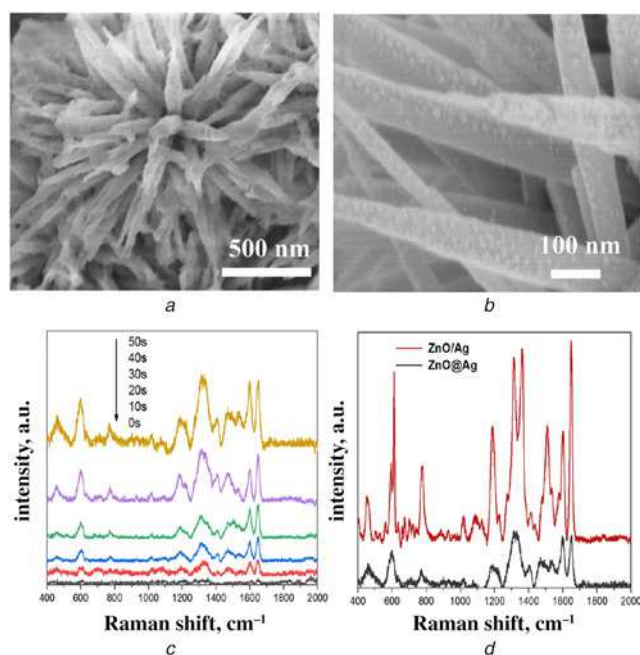


Fig. 5 The SEM images and SERS spectra of samples
 a, b SEM images of ZnO@Ag microflowers where the Ag was fixed at ZnO microflowers by ion beam sputtering for 50 s
 c SERS spectra of Rh6G (10^{-5} M) collected on as-prepared ZnO@Ag microflowers (0–50 s)
 d SERS spectra of Rh6G (10^{-5} M) collected from a ZnO@Ag microflowers (50 s) based substrate and ZnO/Ag microflowers

ratio and large surface area of ZnO nanostructures, which will contact more Ag NPs on the surface of ZnO microflower to form ZnO/Ag microflowers [23]. Therefore, the coupling interaction between closely spaced Ag NPs will induce large electromagnetic field, which serves as the hot spots to enhance the SERS signal.

Moreover, to explain the mechanism of the SERS enhancement, the electromagnetic distribution of ZnO/Ag microflowers was simulated by FDTD method. As shown in Fig. 4c, ZnO/Ag microflowers were composed of Ag NPs and ZnO microflower, with the diameters of 50 nm and 3 μm , respectively. The excitation light was 532 nm. It was clear that there were large electromagnetic enhancements between the junctions of Ag NPs on the wealthy corners and edges of ZnO/Ag microflowers, which attributed to the excellent SERS activity for the detection of Rh6G probes.

As a contrast, the other method such as ion beam sputtering was also employed to deposit Ag NPs on the surface of ZnO microflowers. In order to investigate the effect of the amounts of Ag NPs on SERS-active substrate, ZnO@Ag microflowers samples with different depositing times ranging from 10 to 50 s were prepared. As shown in Figs. 5a and b, Ag NPs were evaporated on the ZnO microflowers successfully. The prepared samples with different deposition times were tested for the SERS activity using Rh6G (10^{-5} M) as a probe molecule. As observed in Fig. 5c, Raman signal peaks were enhanced. Furthermore, Fig. 5d showed the comparison of SERS spectra of ZnO@Ag microflowers (50 s) and ZnO/Ag microflowers. The SERS intensity of ZnO/Ag microflowers were more than four times compared with ZnO@Ag microflowers (50 s). According to the SEM images of ZnO/Ag microflowers (Fig. 3d) and ZnO@Ag microflowers (Fig. 5b), the size and density of Ag NPs on the surface of ZnO/Ag microflowers were large, which resulted in strong coupling interaction and induced remarkable electromagnetic field enhancement between the adjacent Ag nanoparticles. Thus, the SERS activity of ZnO/Ag microflowers was enhanced greatly.

4. Conclusion: In summary, a simple and facile method has been demonstrated for the controllable and reproducible fabrication of 3D microflower-like ZnO@Ag hybrids for SERS. Maximum SERS was realised in the ZnO/Ag microflowers, derived from its wealthy corners and edges with lots of Raman hot spots. Furthermore, the size of the Ag NPs greatly made an impact on the density of the hot spots between the adjacent Ag NPs on both the same ZnO petals and adjacent ZnO petals. The demonstrated microflower-like ZnO@Ag hybrids design provides an attractive and instructive model of structural engineering of semiconductor-metal hybrids serving as highly active and stable SERS sensor for organic molecules detection.

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